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MANGAT, Pal and OJEDOKUN, Olalekan (2019). Bound chloride ingress in alkali activated concrete. Construction and Building Materials, 212, 375-387.

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Bound chloride ingress in alkali activated concrete

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Abstract

Alkali activated cementitious material (AACM) concrete and conventional concrete specimens of similar strength, developed for structural applications, were exposed to a 5% NaCl solution. Bound chloride concentrations (water and acid soluble) were determined up to 270 days of chloride exposure. Chloride diffusion profiles with depth and diffusion parameters C_0 and D_c were derived from the data for water soluble, acid soluble and total bound chloride concentrations in order to develop long term chloride prediction relationships. The results show that the practice of using acid soluble chloride data for long term chloride predictions in conventional concrete is not valid for AACMs due to their low chemical binding capacity. Instead the physically bound chloride (water soluble) is more predominant in AACMs and is suitable for the chloride prediction models. Therefore, relationships of chloride diffusion parameters C_0 and D_c with time have been derived for water soluble chloride. These correlate with total bound chlorides and are suitable for long term predictions of chloride concentrations for the design and maintenance of AACM concrete structures against corrosion.

Keywords: Alkali activated cementitious material AACM; water soluble chloride; acid soluble chloride; bound chloride; surface chloride concentration; chloride diffusion coefficients; chloride prediction models.

Notations:

AACM	alkali activated cementitious material
PC	Portland cement
GGBS	ground granulated blast-furnace slag
SRA	shrinkage reducing admixture
R42	retarder
V_1	ammonium thiocyanate solution used in the first titration [ml]
V_2	ammonium thiocyanate solution used in the second titration [ml]
m	mass of the binder [g]
f	molarity of silver nitrate solution
x	distance from concrete surface (m)
t	time (seconds)
D_C	diffusion coefficient (m^2/s)
$(D_C)as$	acid soluble diffusion coefficient (m^2/s)
$(D_C)ws$	water soluble diffusion coefficient (m^2/s)
$(D_C)tb$	total bound diffusion coefficient (m^2/s)
C_0	surface chloride concentration (% wt. of binder)
C_{as}	acid soluble chlorides (% wt. of binder)
$(C_0)_{as}$	acid soluble surface chlorides (% wt. of binder)
$(C_0)_{ws}$	water soluble surface chlorides (% wt. of binder)
$(C_0)_{tb}$	total bound surface chlorides (% wt. of binder)
$(C_0)_{as,\,180}$	acid soluble surface chlorides at 180days exposure (% wt. of binder)
$(C_0)_{ws,\,180}$	water soluble surface chlorides at 180days exposure (% wt. of binder)
$(C_0)_{tb,\,180}$	total bound surface chlorides at 180days exposure (% wt. of binder)
$C_{(x,t)}$	chloride concentration at distance x and time t .

$(C_{20})_{as}$	acid soluble chloride at 20mm depth (% wt. of binder)
$(C_{20})_{ws}$	water soluble chloride at 20mm depth (% wt. of binder)
$(C_{25})_{as}$	acid soluble chloride at 25mm depth (% wt. of binder)
$(C_{25})_{ws}$	water soluble chloride at 25mm depth (% wt. of binder)
$NaOH$	sodium hydroxide
$NaCl$	sodium chloride
$NaNO_3$	sodium nitrate
ISE	ion selective electrode
C_3A	tricalcium aluminate
C_4AF	tetracalcium aluminate
$Ca_6Al_2O_6.CaCl_2.10H_2O$	Friedel's salt
D_{ref}	diffusion coefficient at reference time t
t_{ref}	reference age (days)
m	age factor
C_{ref}	surface chloride concentration corresponding to the time t_{ref}
k	constant for surface chloride concentration

1.0 Introduction

Alkali activated cementitious materials (AACMs) which do not use the traditional Portland cement (PC) are the basis of alkali activated (AACM) concrete. There is growing interest in the use of alkali activated concrete as a viable alternative to conventional Portland cement (PC) concrete due to its superior sustainability credentials and high performance such as fire resistance [1] and durability properties such as chemical resistance [2]. Considerable information on the sustainability of AACM concrete is available in literature which shows a lower CO_2 emission [3] and energy consumption [4] than PC concrete. However, there is strong resistance to the use of steel reinforced AACM concrete in significant structural applications until its resistance to chloride and carbonation induced corrosion is proven and its design procedures for corrosion resistance are established. The lack of standards has also been a critical limiting factor in the use of AACMs in practice, however, the publication of PAS 8820:2016 [5] starts to overcome this problem.

Serious chloride-induced corrosion damage is common in conventional (PC) reinforced concrete structures exposed to the marine environment and to de-icing salts, such as bridge decks. For example, the annual cost of the maintenance and repair of existing bridges in the US is estimated to be about $12billion [6]. Chloride ingress in AACM concrete is also a major durability concern because it will cause corrosion of steel reinforcement embedded in it [1,7]. The presence of chloride ions in conventional Portland cement (PC) concrete above the established threshold limits [8] cause corrosion of steel reinforcement, however, these threshold limits have not yet been determined for AACM concrete to enable its design for corrosion resistant structures.

The three forms of chloride present in Portland cement (PC) concrete are water soluble, acid soluble and free chlorides [9,10]. A recent study on AACM concrete suggests a considerable reduction in the acid soluble (chemically bound) chloride present within its matrix especially in low calcium systems [7]. However, these chloride concentration properties need to be quantified for different precursors such as high calcium systems and for engineering mixes of AACM concretes to establish threshold levels which initiate reinforcement corrosion. The balance between the three forms of chlorides present in AACMs and the factors involved requires further research. The reaction products and hardening process of AACMs are different from the hydration products of conventional PC concrete [11]. These products play a decisive role in chloride ingress. The differences in the water and acid soluble chlorides between AACM and PC concrete need to be quantified to determine their relative chloride binding properties. Determining the relationship between the bound, free and total chloride in AACM concrete will provide a clearer understanding of chloride induced corrosion of reinforcement in AACM concrete. The possibility of a reduction in the bound chlorides in AACM concrete raises potential concerns about its corrosion resistance.

The ingress of chloride in concrete is a complex interaction of both physical and chemical processes which are predominantly affected by the physical and chemical composition of the cement gel structure [12]. The chloride concentration profiles with depth of concrete exposed to a chloride environment, chloride diffusion coefficients D_c, surface chloride concentrations C_0, are the properties and parameters used to assess the resistance of concrete to long term chloride ingress. These parameters are derived from Fick's second law of diffusion [13] in conventional PC concrete. However, the chloride diffusion parameters such as D_c, C_0 and chloride concentration profiles for practical AACM concrete mixes need to be established to realise their field applications. Research has shown that the apparent chloride diffusion coefficient D_c of PC concrete decreases with time t, indicating a progressive reduction in the rate of chloride diffusion [14,15]. The chloride diffusion in PC concrete is influenced by its physical properties and chloride binding capacity and their effect is represented by the age factor [14,15]. AACM concrete has the potential to provide greater chloride resistance and a more durable construction material due to its distinctive refined pore structure [16].

This paper presents an investigation on the water and acid soluble chlorides which represent the physically and chemically bound chlorides to the binder gel of high calcium (ggbs based) AACM concretes. It quantitatively differentiates the water and acid soluble chlorides under long term chloride exposure of AACM concrete mixes developed for structural applications. Direct chloride diffusion (bulk diffusion) tests under exposure to a chloride solution have been carried out to obtain long term data. Rapid chloride diffusion-cell tests developed for PC concrete [17] are not directly suitable for continuous long term monitoring plus their validity has not been proven for AACMs. The differences in the chloride binding properties and their effect on the chemical concentrations of the pore fluid of PC and AACM concrete are likely to affect the result of such tests. The analysis of the long term chloride diffusion test data of this research show that the practice of using acid soluble (chemically bound) chloride data to determine the diffusion parameters of PC concrete [18,19] for its corrosion prediction calculations is not valid for AACM concrete. Instead, water soluble (physically bound) chloride data are shown to be suitable for AACM concrete mixes. These data have been used to determine their chloride diffusion parameters (C_0 and D_c), including the relationships of these parameters with the period of chloride exposure. Expressions have been derived for long term predictions of chloride concentrations for use in the design and maintenance of AACM concrete structures.

2.0 Experimental programme

2.1 Materials

Ground granulated blast furnace slag (GGBS) and CEM 1 cement of grade 42.5R [8] were used as binders for AACM and PC concrete mixes respectively. The chemical composition of GGBS and PC is given in table 1. The AACM binder was activated with a sodium silicate solution of molarity 6.5mol/L and modulus 2% together with NaOH of molarity 4.8mol/L. AACM 1, 2 and 3 mixes were produced by diluting the activator with water at 0%, 3.88% and 7.76% respectively as shown in Table 2, to optimize workability and determine the effect of dilution on chloride diffusion. The liquid/binder ratio of 0.47 was used in the AACM and PC concrete mixes.

10mm uncrushed gravel, 6mm limestone and a medium grade sand of 80% particle size passing 1mm sieve were used as coarse and fine aggregates in this study. The properties and oxide compositions of these aggregates conform to BS 882:1992 [20].

Retarder and shrinkage reducing admixtures were introduced in the AACM concrete mixes in order to improve their workability and setting time (Table 2). The retarder R42 is a blend of high grade polyhydroxycarboxylic acid derivatives while the shrinkage reducing admixture (SRA) is made from Alkyl-ether. Each admixture contained less than 0.1% chloride ion and 3.5% sodium oxide.

Table 1: Chemical composition of Portland cement and GGBS binders

Chemical component	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	Na_2O	TiO_2	P_2O_5	MnO	SO_3
PC (mass %)	11.1	8.35	3.16	64.2	2.09	1.19	0.227	1.88	2.01	2.14	3.64
GGBS (mass %)	28.6	12.4	5.7	42.3	6.1	0.8	0.4	1.78	<0.1	0.3	0.08

Table 2: Composition of AACM 1, 2, 3 and control PC concrete mixes

Mix	Binder Content (%)	Fine Agg. (%)	Coarse Agg. (%)		Liquid/ Binder Ratio	Activator Dilution (%)	R42	SRA
			10mm Gravel	6mm Limestone			(% by weight of binder)	
AACM 1	25	18	29.3	15.7	0.47	0	0.2	0.5
AACM 2	25	18	29.3	15.7	0.47	3.88	0.2	0.5
AACM 3	25	18	29.3	15.7	0.47	7.76	0.2	0.5
Control PC	20	26	28.9	15.5	0.47(w/c)	-	-	-

*R42 is the retarder; SRA is the shrinkage reducing admixture

2.2 Specimen preparation

The fresh AACM and PC concrete were mixed in a 150 kg capacity Cretangle mixer in accordance with BS EN 206:2013+A1:2016 standard [21]. A total of forty concrete slabs with dimensions of 250 x 250 x 75mm were produced for chloride ingress testing, ten slabs for each AACM 1, 2, 3 and PC concrete. The chloride ingress specimens were cured in the laboratory air at 20 ± 2^0C and 65% R.H, for 24hrs with their top surface covered with polythene sheets before demoulding. The hardened concrete was then cured in water (20 ± 2^0C) for 27days after demoulding. The chloride ingress specimens were taken out of water and surface dried after the 28days' curing period. Two coats of bituminous paint were applied to five faces of the slabs except the bottom cast faces (250mm x 250mm) and allowed to dry for 24hrs. The slabs were then immersed in a 5% by weight NaCl solution to expose the uncoated face to chloride diffusion. The higher limit of 5% chloride concentration specified by the standards [22,23] was used to promote accelerated chloride ingress through the exposed uncoated surfaces. The NaCl solution was stirred frequently and replaced every 90 days to maintain uniform concentration. Two slab specimens for each concrete mix were removed from the chloride solution at exposure periods of 55, 90, 120, 180 and 270 days to determine the water and acid soluble chloride concentrations at increments of depth from the face exposed to chloride diffusion.

Twenty four concrete cubes of dimensions 75mm X 75mm X 75mm were produced for compressive strength testing, 12 cubes were cured in water (20 ± 2^0C) and 12 cubes cured in laboratory air (20 ± 2^0C, 65% R.H).

2.3 Test Procedures

2.3.1 Workability and compressive strength

Slump test was performed in accordance with BS EN 12350-2:2009 [24] to determine the workability of fresh AACM and PC concrete. The compressive strength was determined on

75mm concrete cubes at 28days under wet and dry curing regimes. The compressive strength test was performed in accordance with BS EN 12390-3:2009 [25]. The compressive test results reported in Figure 2 are an average value from three cubes.

2.3.2 Chloride diffusion testing

The collection of dry powder samples from the concrete specimens was carried out in accordance with NordTest 443 [22] and DD CEN/TS 12390-11 [23]. At each test age, two 250 x 250 x 75mm concrete specimens were sawn into two equal halves along the longitudinal plane perpendicular to the chloride exposed uncoated face (Fig. 1). Dry powder samples were collected from seven parallel layers at 8, 15, 25, 35, 50 and 65mm depths from the uncoated surface. A minimum of six holes were drilled per each profile depth by means of a hammer drill using 4mm diameter SDS drill bits. The powder samples from each hole were combined to provide approximately 15grams of powder samples per each profile depth for the two specimens of each concrete mix. The powder samples for each depth were sieved and the fine powder passing through the 150µm sieve as shown in Fig. 1 was carefully stored in a self-sealing plastic bag and labelled accordingly. The retained coarse material was discarded while the fine powder samples were subjected to chloride analysis.

a b

Fig. 1: (a) Location of drilled holes perpendicular to the chloride exposed uncoated face. (b) Concrete powder passing and retained on 150µm sieve.

2.3.3 Chloride analysis

A chloride ion selective electrode (ISE) was used to measure the water-soluble chloride concentrations. Five grams of the concrete powder passing through the 150µm sieve was dissolved in 50ml of distilled water. The effective ionic concentration, otherwise known as the chloride ion activity within the concrete powder solution, was buffered with $NaNO_3$ to avoid possible interference by other ions like iodine, bromide, cyanide and sulphide [26]. The procedure was done three times for each powder sample and the coefficient of variance of repeatability was less than 5%. Calibration of the chloride ISE was done by using a pre-prepared 1000 mg/l and 10 mg/l standard NaCl solution before each test.

The acid soluble chloride concentrations in hardened AACM and PC concrete were determined in accordance with BS EN 14629 [18]. Volhard's titration method was used to determine the chloride concentration on the second part of the concrete powder sample obtained at each profile depth from the exposed surface. The acid soluble chloride content, C_{as} was calculated as a percentage of chloride ions by weight of the binder using equation 1.

$$C_{as} = 3.545 * f * \frac{(V_2 - V_1)}{m} \tag{1}$$

Where V_1 is the volume of the ammonium thiocyanate solution used in the first titration [ml]; V_2 is the volume of the ammonium thiocyanate solution used in the second titration [ml]; m is the mass of binder fraction in the concrete powder sample [g]; and f is the molarity of silver nitrate solution [18].

2.3.4 Chloride diffusion parameters

Fick's second law of diffusion was suggested as a suitable model for chloride diffusion in concrete by Collepardi et al. [13], which gives the following equation;

$$C_{(x,t)} = C_0 \left(1 - erf\left[\frac{x}{2\sqrt{D_C}\ t}\right]\right) \quad (2)$$

Where: x is the distance from concrete surface (m); t is the time (seconds); D_c is the diffusion coefficient (m^2/s); C_0 is the chloride concentration on the concrete surface; $C_{(x,t)}$ is the chloride concentration at distance x and time t .

The experimental data of acid and water-soluble chloride concentrations with depth were plotted at every test age. An error function analysis using Fick's second law of diffusion equation 2 was performed on the chloride profiles to determine the constant values of the diffusion parameters C_0 and D_c at each test age. These values were used to determine the age factor which accounts for the change in diffusion coefficients with time [27,28] and can ultimately enable long-term predictions of chloride diffusion in AACM concrete.

3.0 Results and Discussion

3.1 Workability and Compressive strength

The slump of fresh AACM 1, 2, 3 and PC concrete was 30, 45, 70 and 75mm respectively. The workability (slump) of AACMs is lower than the PC concrete due to the sticky characteristics of silicate present in AACMs. However, AACM 3 and PC concrete gave fairly similar workability due to the lower silicate content in the activator used for AACM 3 concrete (7.76% activator dilution).

The 28day compressive strengths of AACM 1, 2, 3 and PC concrete cured in water (20 ± 2^0C) and under dry curing in the laboratory air (20 ± 2^0C, 65% R.H) are shown in Fig. 2.

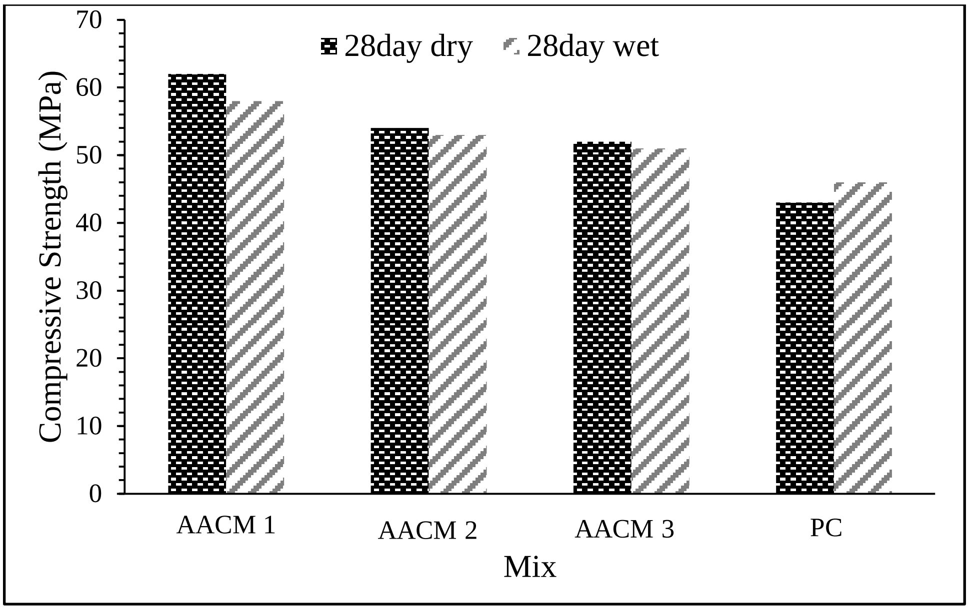

Fig. 2: 28day compressive strength of AACM and PC concrete cured in water (20 ± 2^{0}C) and laboratory air (20 ± 2^{0}C, 65% R.H).

AACM concrete mixes had greater strength than PC concrete under wet and especially dry curing. AACM 3 has a similar workability as the PC concrete and their strength difference under wet curing is within 10%. The two mixes have the same liquid/binder and water/cement ratios of 0.47 respectively. The PC concrete provides the control specimen for AACM 3 since wet curing is the standard quality control criteria for concrete. The 28day strength of AACM 3 concrete under dry curing is 18% higher than PC concrete.

AACM 1 concrete with the highest activator concentration resulted in the highest strength due to higher reaction rate and the formation of a less porous matrix [16]. For example, the 28-day compressive strength of AACM 1 (0% activator dilution) and AACM 3 (7.76% activator dilution) was 62MPa and 52MPa respectively, under dry curing (Fig. 2).

3.2 Chloride diffusion profiles

3.2.1 Water soluble chloride

The profiles in Fig. 3 represent the water soluble chloride concentrations (% weight of binder) along the depth (0-75mm) of the specimens. A non-linear regression analysis was performed on the experimental data plotted in Figures 3 and 4 using Fick's second law of diffusion equation 2 and the best-fit lines are plotted using excel software. The regression analysis also provided the values of the diffusion coefficient D_c and surface chloride concentration C_0 at each exposure age. Discussion on the diffusion coefficient D_c and surface chloride concentration C_0 will follow in section 3.4.

The chloride profiles of AACM 1, 2, 3 and the control PC concrete at 55 and 180days exposure periods are shown in Fig. 3 while Fig. 4 shows chloride concentrations in the concrete cover zones (20 and 25mm depths) for exposure periods of 55, 90, 120 and 180days. The 20 and 25mm depths represent the concrete cover zone which could be higher (up to 50mm) in marine structures. However, the exposure period represented in Figures 3 and 4 is not sufficiently long-term to provide detectable differences at higher depths. Figure 4 shows a linear increase in water-soluble chloride concentrations with longer chloride exposure. The coefficient of correlation for the best-fit lines in Figures 3 and 4 ranged between 0.81 and 0.99.

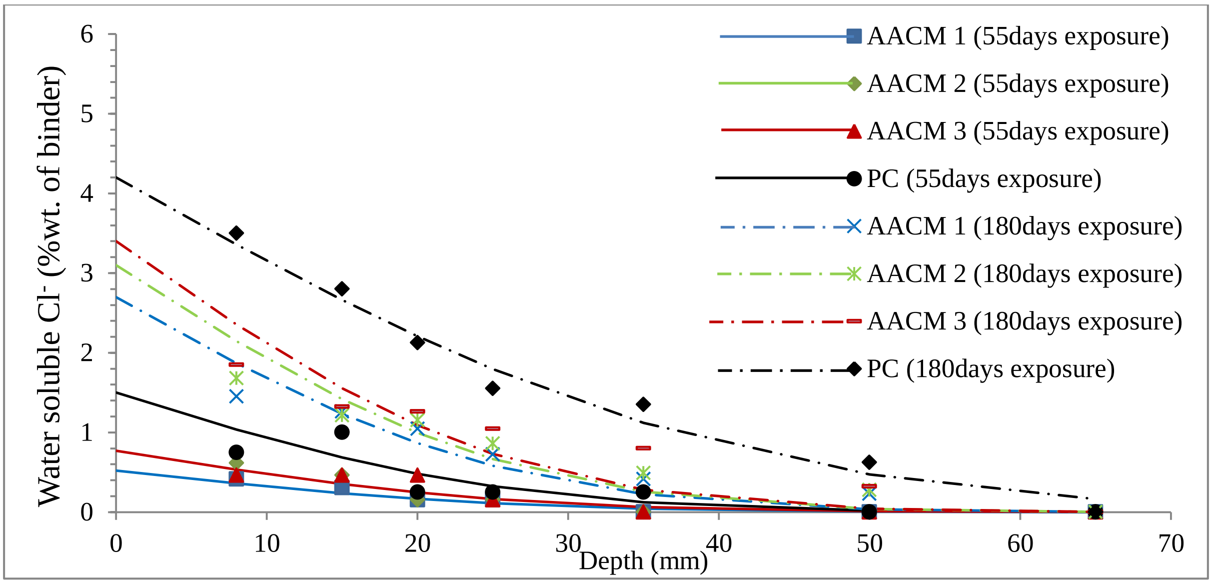

Fig. 3: Water soluble chloride profiles of AACM 1, 2, 3 and control PC concrete at 55 and 180 days of chloride exposure.

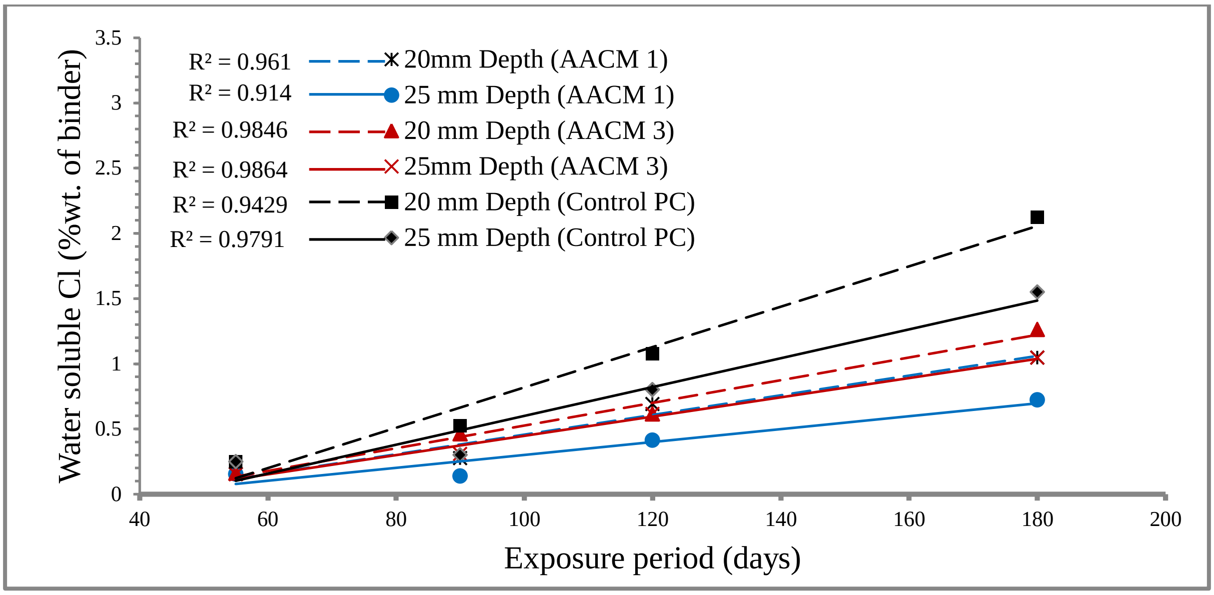

Fig. 4: Relationship between water soluble chlorides (20 and 25mm depth) and exposure period of AACM 1, 3 and control PC concrete

A lower water-soluble chloride profile is exhibited by AACM 1, 2 and 3 concrete than the control PC concrete at 55 and 180 days of chloride exposure (Fig. 3). For example, at 25mm depth, the chloride concentration of AACM 3 concrete at 180days exposure is 1.05% by weight of binder compared with 1.55% by weight of binder in PC concrete. Both of these values are significantly greater than the corrosion threshold chloride concentrations given in standards [8], which are 0.4% and 1.0% by weight of binder for concrete with and without steel reinforcement respectively. This is due to the accelerated chloride diffusion test providing continuous immersion in a 5% NaCl solution [23]. The high concentration of NaCl is recommended in international standards [22,23] for comparative evaluation of mixes and for determining diffusion coefficients C_0 and D_c.

The water soluble chloride concentration is lower in AACM 3 compared with its control PC concrete, which becomes more significant with longer exposure (Fig 4) due to greater physical binding of chloride occurring in PC concrete with time.

3.2.2 Acid soluble chloride

Figure 5 shows the experimental data points and the acid soluble chloride profiles of AACM 1, 2, 3 and the control PC concrete at 55 and 270days exposure. Non-linear regression analysis of the experimental data against Fick's 2nd law of diffusion equation 2 gave the chloride profiles plotted in Fig. 5. The coefficients of correlation range between 0.80 and 0.94.

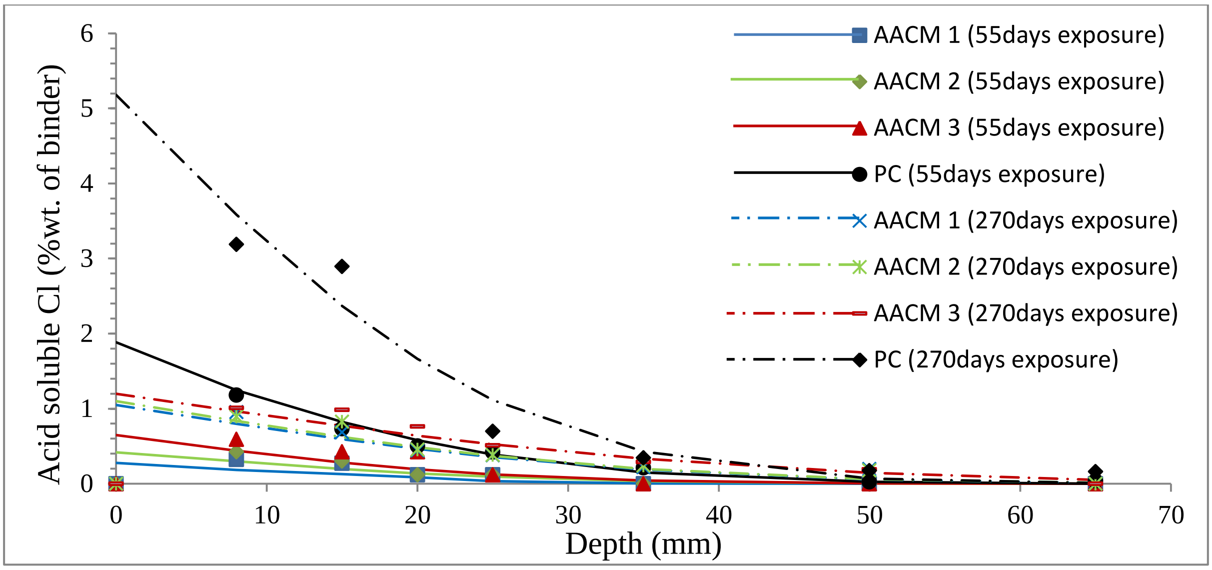

Fig. 5: Acid soluble chloride profiles of AACM 1, 2, 3 and control PC concrete at 55 and 270 days of chloride exposure.

Acid soluble chloride profiles of AACM 1, 2, 3 and the control PC concrete show an increase of chloride concentrations with exposure time, both on the concrete surface and at all depths within the concrete matrix. The profiles of the control PC concrete show much higher chloride concentrations than the AACM 1, 2 and 3 concrete at 55 and 270days exposures (Fig. 5).

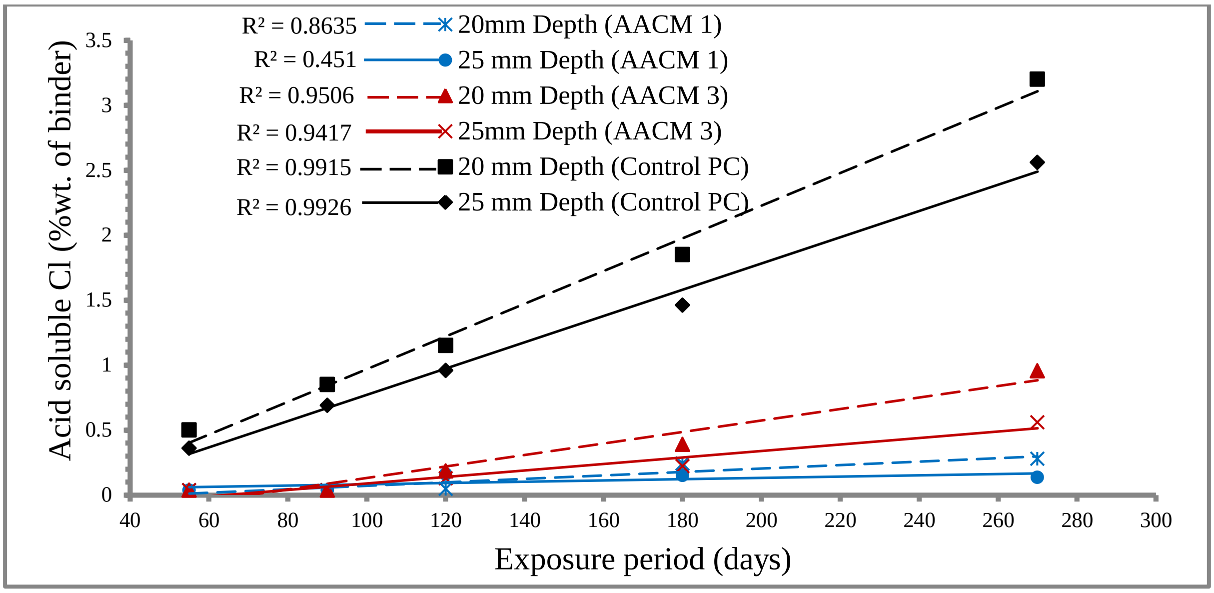

Fig. 6: Relationship between acid soluble chlorides (20 and 25mm depth) and exposure period of AACM 1, 3 and control PC concrete

Figure 6 shows the acid soluble chloride concentrations at 20 and 25mm depths in AACM 1, 3 and control PC concrete at exposure periods of 55, 90, 120, 180 and 270days. The acid soluble chloride concentrations of AACM 1 and 3 concrete are much lower than the control PC concrete at different chloride exposure periods with the difference getting bigger with increasing exposure period thereby indicating much higher chemical binding of chloride occurring with time in PC concrete. For example, at 25mm depth, the chloride concentration of AACM 3 concrete at 270days exposure is 0.56% by weight of binder compared with 2.56% in the control PC concrete (Fig. 6). The PC concrete has significantly greater value than the corrosion threshold chloride concentrations given in standards [8] which are 0.4% and 1.0% by weight of binder for concrete with and without steel reinforcement. The chloride threshold values for initiating corrosion given in the standard [8] relate to the total bound and acid soluble chloride in PC concrete. However, neither of these bound chlorides (acid and water soluble) are the direct initiators of corrosion, the free chloride (pore fluid) being the electrolyte which supports corrosion.

3.3 Bound chlorides in AACM and PC concrete

The water soluble, acid soluble and total bound chlorides in AACM 1, 3 and PC concrete at 20mm depth for 55 and 180days exposure are shown in Fig. 7. The corresponding results for 25mm depth are shown in Fig. 8. The total bound chlorides are represented as the sum of water soluble and acid soluble chlorides for the AACM concretes. For PC concrete, the total bound and acid soluble chlorides are taken to be equal as it is generally assumed in literature and testing standards [18,19].

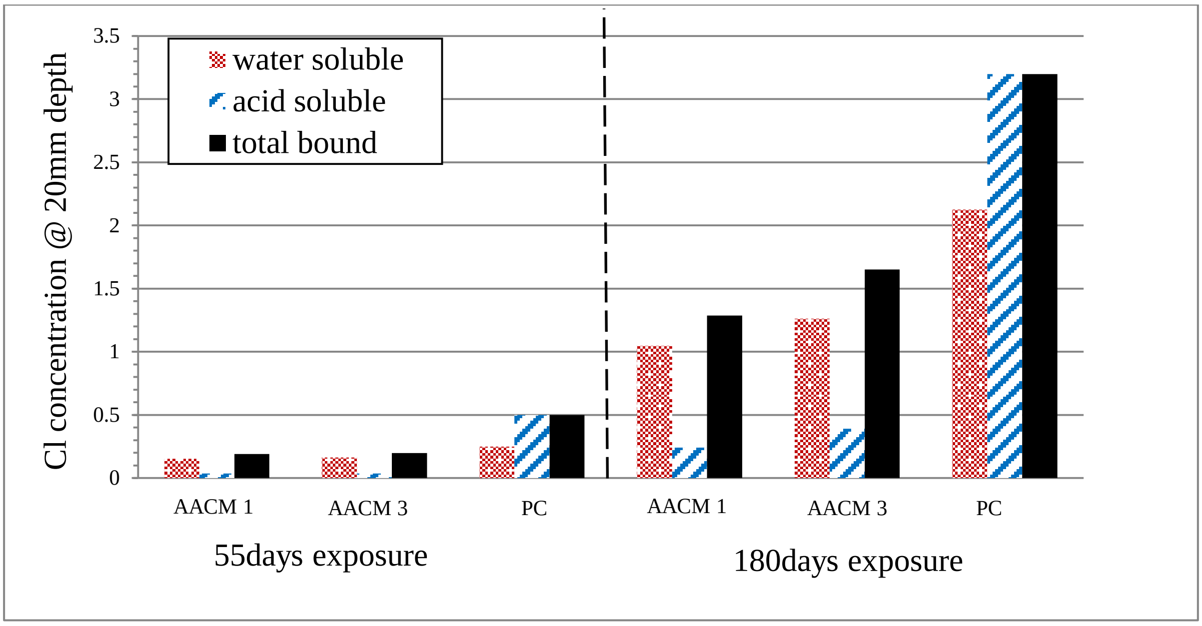

Fig. 7: Water, acid soluble and total bound chlorides at 20mm depth in AACM 1, 3 and control PC concrete at 55 and 180days exposure.

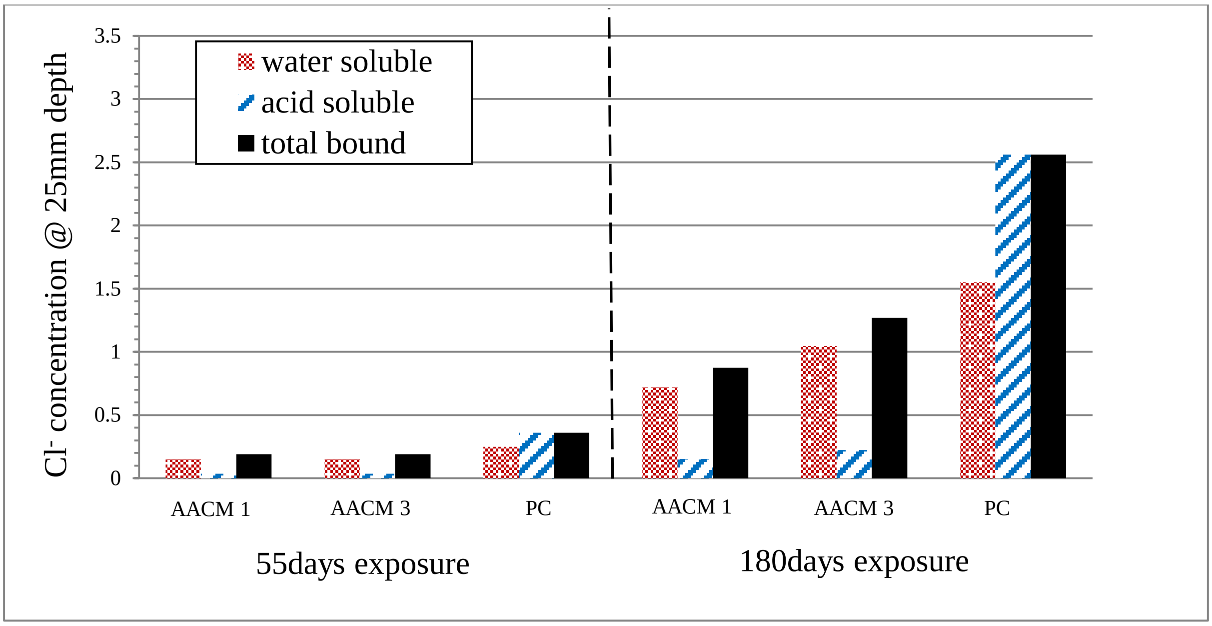

Fig. 8: Water, acid soluble and total bound chlorides at 25mm depth in AACM 1, 3 and control PC concrete at 55 and 180 days exposure.

The acid-soluble chlorides in AACM 1 and 3 concrete are considerably lower than the water-soluble chlorides at both 55 and 180days exposure whereas the reverse is true for the control PC concrete (Figures 7 and 8). For example, the water soluble chlorides of AACM 1 and 3 concrete at 180days exposure are 1.05% and 1.26% compared with 0.24% and 0.39% for acid soluble chlorides at 20mm depth (Fig. 7). The corresponding values for PC concrete are 2.13% for water soluble chloride compared with 3.2% for acid soluble chloride at 20mm depth. A similar trend is shown at 25mm depth which is presented in Fig. 8. The significant observations from Figures 7 and 8 show that both water soluble and acid soluble chloride contents in AACM concrete are less than the PC concrete. However, the reduction is much greater in acid soluble chloride. The acid soluble chloride content in AACM concrete is much lower than its water soluble chloride content, whereas it is the opposite in PC concrete.

The above observations indicate that the balance between chemical and physical binding of chlorides in the matrix is different in PC and AACM concretes. The total bound chloride content in Figures 7 and 8 comprises of the physically bound (water soluble) and chemically bound (acid soluble) chlorides. Conventional PC concrete shows higher chemical binding than physical binding due to the C_3A and C_4AF in its PC binder. The unhydrated portion of aluminate (C_3A) and aluminoferrite (C_4AF) of PC binders reacts with the chloride ions in the pore solution during the exposure period, transforming it to Friedel's salt ($Ca_6Al_2O_6.CaCl_2.10H_2O$) and calcium chloroferrite [29]. This is responsible for the increase in acid soluble chloride concentration in PC concrete with longer exposure period. The hydration reaction of aluminate (C_3A) and aluminoferrite (C_4AF) that takes place before the exposure of PC concrete to NaCl solution does not contribute to its acid soluble chlorides [29]. The lack of aluminate (C_3A) and aluminoferrite (C_4AF) in the AACM compositions of Table 1 results in low chemically bound chlorides (acid soluble) in the AACM matrix.

Therefore, unlike PC concrete, AACM concrete has higher physical binding capacity than its chemical binding capacity. The chloride binding capacity of concrete is an important property that regulates the amount of free chlorides in the concrete matrix, which initiate corrosion when their permissible limits are exceeded.

3.4 Chloride diffusion parameters (C_0 and D_c)

3.4.1 Long term C_0 and D_c models

The solution of Fick's 2nd law of diffusion, $\delta C/\delta t = D\ \delta^2 C/\delta x^2$, which is given in equation 2 assumes a constant value for the chloride diffusion parameters (C_0 and D_c). However, research has shown that these coefficients vary with time [14,15,27,28] due to changes in the properties of concrete with time, such as porosity and chloride binding in concrete. These effects are represented by the age factor, m, of concrete [30]. Research on the long-term diffusion coefficient of concrete, D_C, has derived an empirical relationship in the form of a power function given in equation 3 [15,28].

$$D_C = D_{ref}\, t^{-m} \qquad 3$$

where: D_c is the apparent diffusion coefficient at time t, D_{ref} is diffusion coefficient at reference time t and m is the age factor.

A theoretical solution based on Fick's second law of diffusion which takes account of the time variation of the diffusion coefficient by introducing the age factor, m, from equation 3 has been derived elsewhere [15,28] and given in equation 4.

$$C_{(x,t)} = C_{(0)}\left(1 - erf\left[\frac{x}{2\frac{\sqrt{D_{ref}\, t^{(1-m)}}}{\sqrt{1-m}}}\right]\right) \qquad 4$$

Similarly, the time dependent C_0 has been shown to be proportional to the square root of chloride exposure period [31,32], and the relationship is given in (Eqn. 5)

$$C_0 = C_{ref} + k\sqrt{t - t_{ref}} \qquad 5$$

Where C_{ref} and t_{ref} are reference surface chloride and the reference time (=55days) respectively, k and m are the age factors influencing the long-term surface chloride concentrations and diffusion coefficients respectively, C_0 is the chloride concentration on the concrete surface, $C_{(x,t)}$ is the chloride concentration at distance x and time t.

The following analysis given in the paper uses the chloride diffusion data at each test age (55, 90, 120, 180 and 270days) to determine C_0 and D_c values using equation 2. The values of coefficient m and k have been determined by regression analysis of the plots of C_0 and D_c against exposure time.

3.4.2 Surface chloride concentration C_0

The surface chloride concentrations, C_0, were calculated at each age by applying the Fick's 2nd law of diffusion (equation 2) to all the chloride diffusion data obtained at 55, 90, 120 and 180days exposure to the chloride solution. The C_0 values are plotted in Figure 9 and a regression analysis by applying equation 5 have been carried out to determine relationships for long term predictions of C_0 for each concrete mix. Fig. 9 shows the relationship between the chloride exposure period term $(t-t_{ref})^{0.5}$ and water soluble $(C_0)_{ws}$, acid soluble $(C_0)_{as}$, total bound $(C_0)_{tb}$ surface chlorides. Similar relationships exist for the data of AACM 1 and 2.

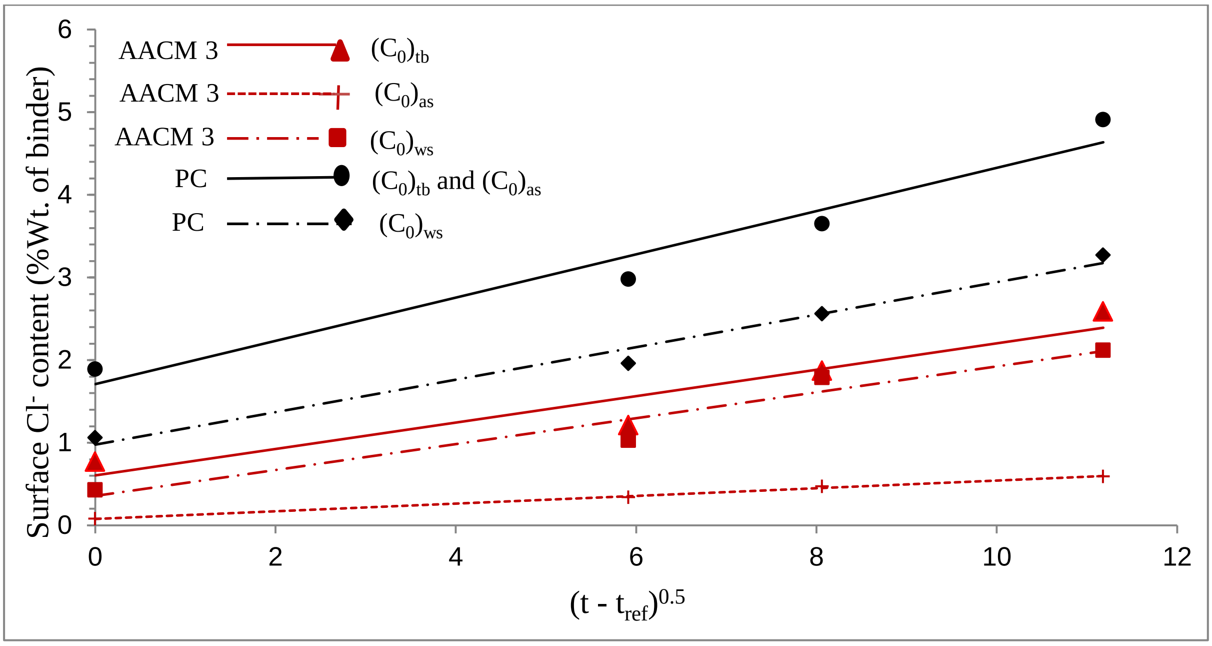

Fig. 9: Relationship between *$(C_0)_{ws}$, $(C_0)_{as}$, $(C_0)_{tb}$* and chloride exposure period for AACM 3 and PC concrete.

The linear equations between C_0 and $(t - t_{ref})^{0.5}$ for AACM 1, 2, 3 and PC concrete and their level of correlation are presented in Table 3. The surface chloride concentration at 180days exposure, $(C_0)_{180}$, obtained from each equation is also listed in Table 3.

Table 3: Relationships of $(C_0)_{ws}$, $(C_0)_{as}$, $(C_0)_{tb}$ with chloride exposure period $(t - t_{ref})^{0.5}$

Mix	Surface Cl^- (C_0)	Linear equation	R^2	$(C_0)_{180}$ (%wt. of binder)
AACM 1	tb	$(C_0)_{tb} = 0.134(t-t_{ref})^{0.5} + 0.24$	0.97	1.74
	as	$(C_0)_{as} = 0.034(t-t_{ref})^{0.5} + 0.028$	0.98	0.41
	ws	$(C_0)_{ws} = 0.13(t-t_{ref})^{0.5} + 0.12$	0.95	1.57
AACM 2	tb	$(C_0)_{tb} = 0.139(t-t_{ref})^{0.5} + 0.52$	0.97	2.07
	as	$(C_0)_{as} = 0.039(t-t_{ref})^{0.5} + 0.06$	0.99	0.50
	ws	$(C_0)_{ws} = 0.134(t-t_{ref})^{0.5} + 0.25$	0.96	1.75

AACM 3	tb	$(C_0)_{tb} = 0.16(t\text{-}t_{ref})^{0.5} + 0.60$	0.90	2.39
	as	$(C_0)_{as} = 0.046(t\text{-}t_{ref})^{0.5} + 0.08$	0.99	0.60
	ws	$(C_0)_{ws} = 0.157(t\text{-}t_{ref})^{0.5} + 0.36$	0.94	2.11
PC	tb and as	$(C_0)_{tb}$ and $(C_0)_{as} = 0.262(t\text{-}t_{ref})^{0.5} + 1.71$	0.96	4.64
	ws	$(C_0)_{ws} = 0.197(t\text{-}t_{ref})^{0.5} + 0.98$	0.98	3.18

Where: $(C_0)_{tb}$, $(C_0)_{as}$ and $(C_0)_{ws}$ are total bound, acid soluble and water soluble chlorides respectively, t is the exposure time (days) and t_{ref} is the reference exposure time (55days).

The values of $(C_0)_{180}$ in Table 3 show that for PC concrete, the $(C_0)_{tb,180}$ and $(C_0)_{as,180}$ are both equal to 4.64% wt. of binder. The corresponding $(C_0)_{ws,180}$ is much lower at 3.18% wt. of binder. Therefore, both total bound and acid soluble chloride data are suitable for long term chloride prediction for PC concrete. This conforms with current practice where test procedures used for chloride ingress in PC concrete determine acid soluble chlorides only [18,19] and these values are used in long term prediction models [14,15,27,28].

However, the data in Table 3 show that the $(C_0)_{tb,180}$ and $(C_0)_{as,180}$ for AACM 3 concrete are very different at 2.39% and 0.60% wt. of binder respectively. The acid soluble chloride values are too low to be suitable for long term chloride predictions and, therefore, the acid soluble chloride test procedure is not valid for AACMs.

The water soluble surface chloride $(C_0)_{ws,180}$ of the AACM 3 mix in Table 3 is 2.11% wt. of binder compared to 2.39% wt. of binder for $(C_0)_{tb,180}$. Their difference is within 15% and potentially the $(C_0)_{ws,180}$ values could be used for long term predictions of chlorides in AACM concrete. The accuracy of this approach will be determined in section 3.4.4.

The $(C_0)_{as,180}$ and $(C_0)_{ws,180}$ values are 0.60% and 2.11% wt. of binder respectively for AACM 3 (Table 3). The very low acid soluble chloride shows that a higher proportion of the chloride is being physically bound to the walls of the binder gel in AACMs than forming chemically bound chloride compounds during geopolymerisation.

Higher $(C_0)_{ws}$, $(C_0)_{as}$ and $(C_0)_{tb}$ are observed in PC concrete than AACM 3 concrete. For example, the $(C_0)_{ws}$, $(C_0)_{as}$ and $(C_0)_{tb}$ at 180days exposure are 3.18%, 4.64% and 4.64% by weight of binder respectively for PC concrete while it is 2.11%, 0.60% and 2.39% for AACM 3 concrete. Both the $(C_0)_{ws}$ and $(C_0)_{as}$ of the control PC concrete are significantly higher than AACM 3 concrete, which represents higher physical and chemically bound chlorides in PC concrete. These $(C_0)_{as}$ values of PC concrete are in a similar range of 1.1% to 7.2% by binder weight given in literature from other research [33–36]. However, existing literature lacks comparative data for AACM concrete.

3.4.3 Chloride diffusion coefficient D_c

Equation 2 has been applied to all the chloride diffusion data to determine the chloride diffusion coefficients at each test age by a non-linear regression analysis. The regression equations and their coefficients of correlation are given in Figures 10 and 11. Figure 10 shows the relationship between acid soluble chloride $(D_c)_{as}$ and chloride exposure period for AACM 1, 2, 3 concrete, whereas the graph for PC concrete in Fig 10 represents $(D_c)_{ws}$ instead of $(D_c)_{as}$. Fig. 11 shows the the relationship of both total bound chloride $(D_c)_{tb}$ and water soluble chloride $(D_c)_{ws}$ against chloride exposure period for AACMs. However, the graph for PC concrete in Fig. 11 represents the $(D_c)_{as}$ instead of $(D_c)_{ws}$.

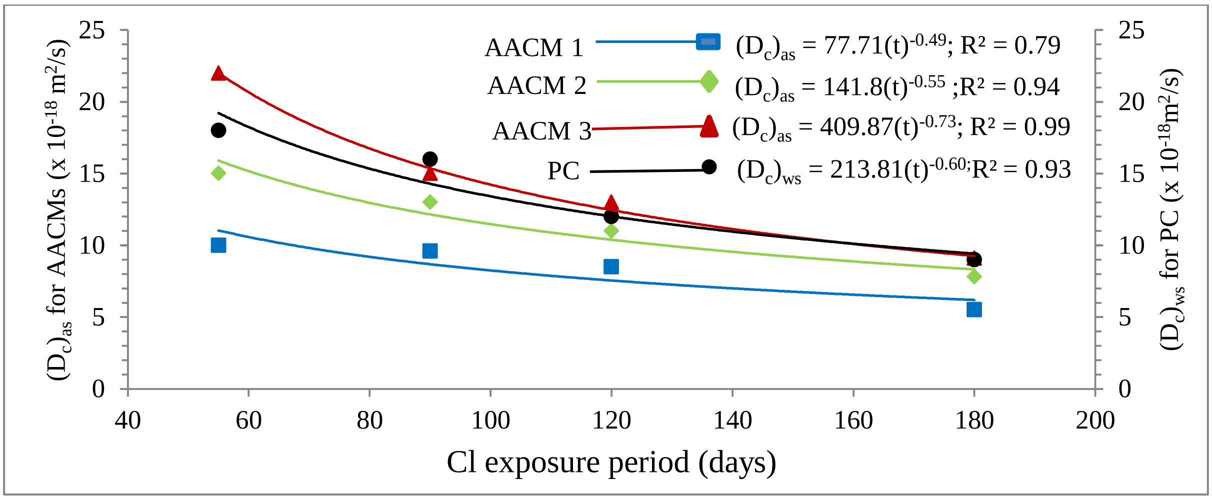

Fig. 10: Relationship of $(D_c)_{as}$ for AACMs and $(D_c)_{ws}$ for PC versus Cl^- exposure period

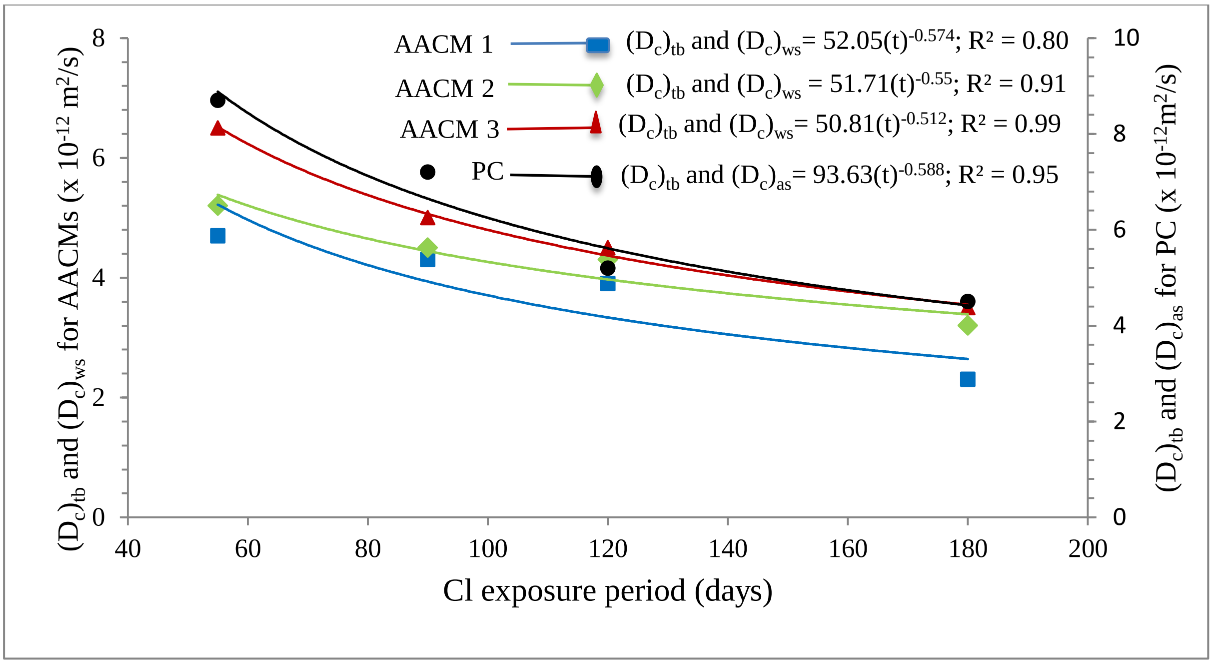

Fig. 11: Relationship of $(D_c)_{tb}$, $(D_c)_{ws}$ for AACMs and $(D_c)_{tb}$, $(D_c)_{as}$ for PC concrete versus Cl$^-$ exposure period

Chloride diffusion coefficient, D_c, values for AACMs given in literature are mainly based on rapid chloride penetration test RCPT. Since the pore fluid and bound chloride properties of AACMs and PC are different, this affects the migration of chlorides. The validity of these tests to AACMs needs to be verified. The D_c values given in literature for AACMs usually relate to the acid soluble $(D_c)_{as}$ which are assumed to represent total bound $(D_c)_{tb}$ [18,19]. This results in an under estimation of the total bound $(D_c)_{tb}$ in AACMs. The graphs in Figures 10 and 11 show that the acid soluble chloride $(D_c)_{as}$ values of AACM concretes (Fig. 10) are orders of magnitude lower (10^{-18} against 10^{-12}) than their total bound chloride $(D_c)_{tb}$ values (Fig. 11) unlike PC concrete which has the same $(D_c)_{as}$ and $(D_c)_{tb}$ values of 4.5 x 10^{-12}m^2/s at 180days exposure (Fig. 11). Therefore, the procedures and test standards adopted for PC concrete using acid soluble chlorides [18,19] are not valid for AACMs.

On the other hand, the water soluble chloride $(D_c)_{ws}$ values of AACMs are the same as their total bound chloride $(D_c)_{tb}$ as shown in Fig. 11. For example, both the water soluble $(D_c)_{ws}$ and total bound $(D_c)_{tb}$ for AACM 1, 2 and 3 are 2.3 x 10^{-12}m^2/s, 3.2 x 10^{-12}m^2/s and 3.5 x 10$^-$

$^{12}m^2/s$ respectively at 180days chloride exposure. Therefore, the water soluble $(D_c)_{ws}$ in AACMs instead of $(D_c)_{as}$ are representative of the diffusion coefficient of AACMs as they equal the total bound $(D_c)_{tb}$.

The chloride induced corrosion prediction of AACM concrete structures requires reliable chloride diffusion parameters (D_c and C_0). The values based on total bound chlorides or equivalents should be used to determine the diffusion coefficients. Diffusion coefficients in literature (and in practice) are usually determined from acid soluble chloride data without considering the water soluble chlorides. This approach gives an incorrect assessment for AACM concrete because, as shown in Figures 9-11, the greater amount of chloride concentration is neglected when using $(D_c)_{as}$. Therefore, the test standards [18,19] for conventional PC concrete, which are based on acid soluble chloride measurements, are not suitable for AACMs. They need to be revised, focusing on water soluble chlorides.

3.4.4 Long term prediction of D_c, C_0 and Cl^- content

3.4.4.1 Chloride diffusion coefficients D_c

Time dependent models for D_c and C_0, based on equations 3 and 5 [31,32], were used to predict long-term (20years) chloride diffusion parameters and chloride concentrations to determine the relative accuracy of predictions for AACM concrete using water soluble and total bound chloride data. Figure 12 shows the experimental data of (D_c) up to 270days exposure and predicted values beyond this age. The age factor m in equation 3 was derived by a regression analysis of the experimental data in Figure 10 and 11 for each AACM concrete. These values are used to predict the long-term total bound $(D_c)_{tb}$, acid soluble $(D_c)_{as}$ and water soluble $(D_c)_{ws}$ for 20years chloride exposure period as shown in Figure 12 and Table 4. The chloride concentrations at 20mm depth after 20years chloride exposure are calculated from equation 2 using the diffusion parameters D_c and C_0 which are calculated from equations 3 and 5.

$$D_C = D_{ref}\, t^{-m} \qquad (3)$$

$$C_0 = C_{ref} + k\sqrt{t - t_{ref}} \qquad (5)$$

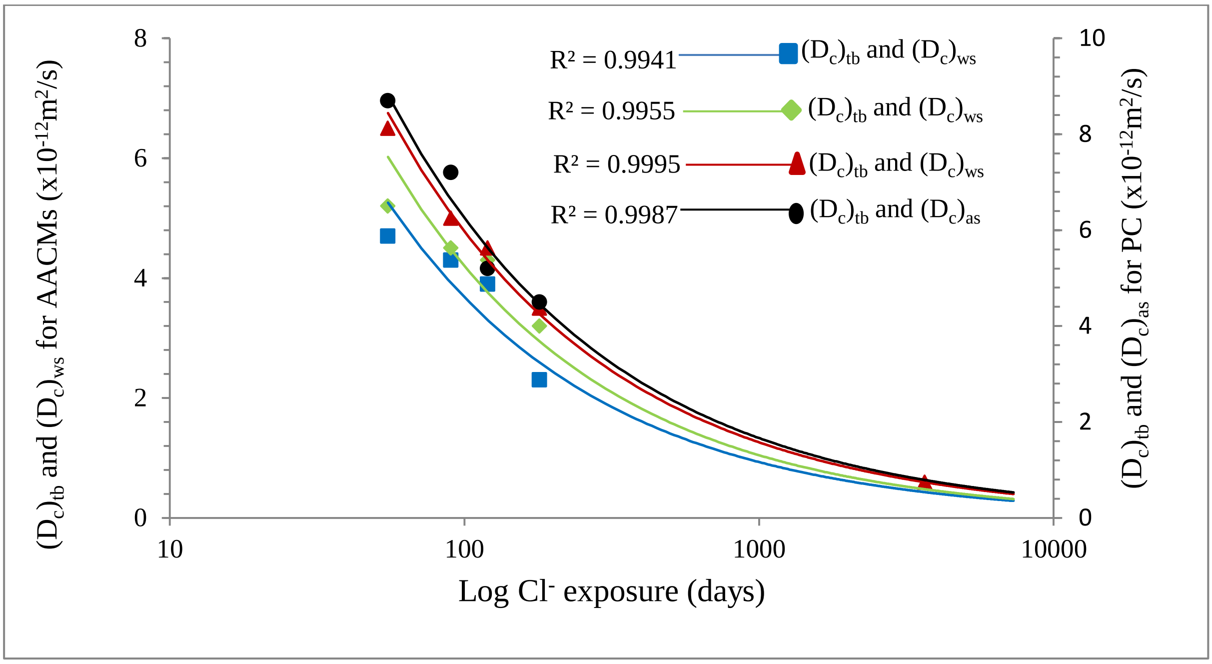

Fig. 12: Chloride diffusion coefficient prediction of AACM and PC concrete up to 20years of Cl^- exposure

All the calculated values at 20years exposure are given in Table 4.

Table 4: Predicted chloride diffusion parameters at 20years exposure

Mix	$(D_c)_{ws}$	$(D_c)_{as}$	$(D_c)_{tb}$	$(C_0)_{ws}$	$(C_0)_{as}$	$(C_0)_{tb}$	$(Cl_{20})_{ws}$	$(Cl_{20})_{as}$	$(Cl_{20})_{tb}$
		(m^2/s)			(%wt. of binder)			(%wt. of binder)	
AACM 1	2.89×10^{-13}	3.67×10^{-19}	2.89×10^{-13}	11.19	2.92	11.65	4.08	0	4.20
AACM 2	3.2×10^{-13}	7.48×10^{-19}	3.2×10^{-13}	11.66	3.38	12.35	4.46	0	4.66
AACM 3	4.0×10^{-13}	9.11×10^{-19}	4.0×10^{-13}	13.72	3.99	14.22	5.26	0	5.54
PC	8.2×10^{-19}	5.36×10^{-13}	5.36×10^{-13}	17.75	24.01	24.01	0	10.68	10.85

3.4.4.2 Surface chloride C_0 and Cl^- content

The equations for C_0 given in Table 3 together with C_0 values based on the experimental data up to 270days exposure are used to plot Fig. 13 to enable long-term predictions of chloride concentrations. The C_0 values at 20years exposure are given in Table 4.

The chloride concentrations at 20mm depth after 20years chloride exposure which are given in Table 4 have been calculated from equation 2 using the diffusion parameters C_0 and D_c given in Table 4.

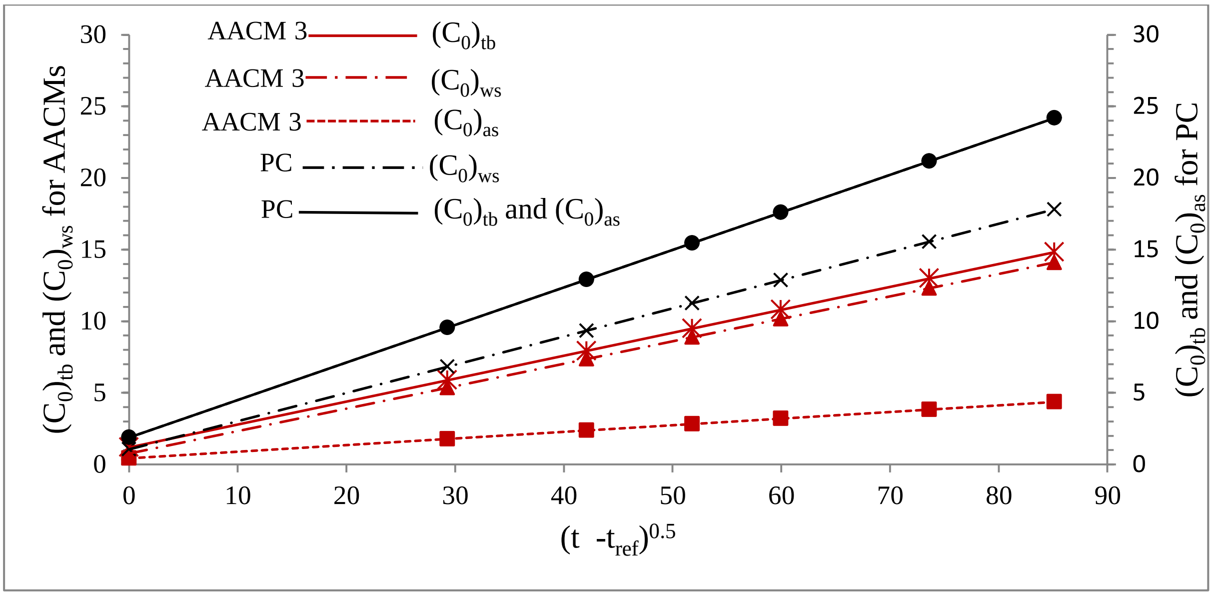

Fig. 13: $(C_0)_{as}$, $(C_0)_{ws}$ and $(C_0)_{tb}$ prediction for AACM 3 and PC concrete up to 20yrs of Cl^- exposure

The results in Table 4 show that the chloride predictions of AACM 1 concrete after 20years chloride exposure gave similar values of 4.08% and 4.20% wt. of binder when C_0 and D_c based on water soluble and total bound chlorides respectively are used in the calculation. The Cl_{20} for AACM 2 and 3 are also similar when water soluble and total bound chloride based C_0 and D_c are used for their calculations. However, the $(Cl_{20})_{as}$ values for the AACM concretes are 0% wt. of binder. Therefore, in practice the data of water soluble chlorides in AACMs can be used to determine their diffusion coefficients for long term chloride predictions. The use of acid soluble chloride data is unsuitable for AACM concretes. These results are contrary to PC concrete for which chloride predictions based on acid soluble chloride data (Table 4) are valid.

3.5 Chloride diffusion parameters and Porosity relationship

The relationships between chloride diffusion parameters (D_c and C_0) and porosity of AACM concrete are shown in Fig. 14. The porosity data at the core of 75mm cube specimens of AACM mortar mixes corresponding to the concrete mixes of this study, with the same binder and activator content (liquid/binder ratio of 0.47) have been reported by the authors previously [16]. The pore properties were determined by mercury intrusion porosimetry.

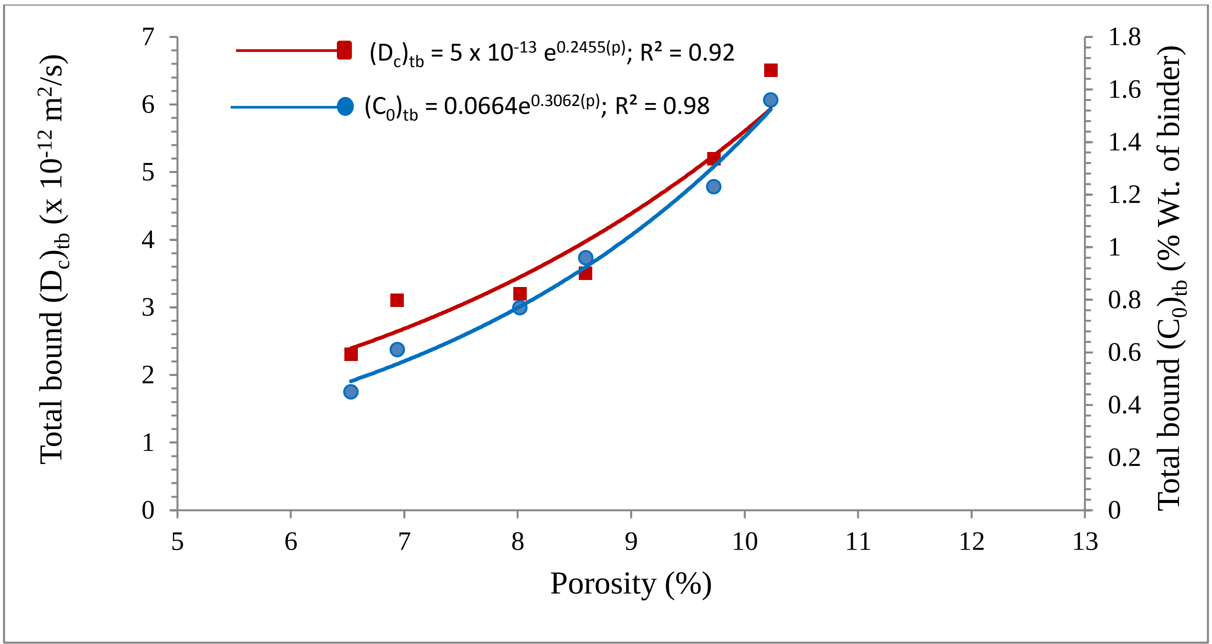

Fig. 14: Relationship between $(D_c)_{tb}$, $(C_0)_{tb}$ and porosity of AACM concrete at 28days.

The relationships between porosity and diffusion parameters of AACM concrete are as follows:

$(C_0)_{tb} = 0.0664e^{0.31(p)}$ with $R^2 = 0.98$.

$(D_c)_{tb} = 5 \times 10^{-13}\ e^{0.25(p)}$ with $R^2 = 0.92$.

Where; $(C_0)_{tb}$ and $(D_c)_{tb}$ are the total surface chloride (% wt. of binder) and diffusion coefficient (m^2/s) respectively and p is the porosity (%).

The chloride diffusion parameters C_0 and D_c depend on a number of factors such as the chloride concentration of the exposure solution, porosity and pore size distribution. These factors differ between AACM and PC concrete which affects the adsorption and absorption of chlorides to the binder gel. The porosity of AACMs is lower than the control PC concrete

[16] and the pore structure is more restricted to chloride diffusion. The relationships of C_0 and D_c with porosity are different for AACMs and PC concrete. The porosity of the control PC mortar mix was 10% with $(D_c)_{tb}$ and $(C_0)_{tb}$ of 4.5 x $10^{-11}m^2/s$ and 5.2% weight of binder respectively, which fall outside the graphs for AACMs in Figure 14.

CONCLUSIONS

This paper investigates chloride ingress in structural grade AACM concretes and a control PC concrete. The concrete mixes were exposed to 5% NaCl solution up to 270 days. The water and acid soluble chlorides in AACM and PC concrete were determined at 55, 90, 120, 180 and 270days exposure. Chloride concentration profiles with depth were determined and chloride diffusion parameters such as surface chloride concentration and chloride diffusion coefficient were calculated to enable long term chloride predictions. The following conclusions can be drawn from the study.

1. The water and acid soluble chloride concentrations in AACM concrete increase with exposure period. Both chloride concentration profiles with depth show good correlation with Fick's second law of diffusion.

2. AACM concrete shows a greater increase with time in water-soluble chloride (physically bound chloride) than the acid soluble chloride (chemically bound chloride) while the control PC concrete shows more acid soluble chloride than water-soluble chloride. However, the total bound chloride is greater in PC concrete. For example, the water and acid soluble chlorides at 20mm depth for AACM 3 concrete are 1.26% and 0.39% respectively while they are 2.13% and 3.20% for the control PC concrete at 180days chloride exposure. The total bound chlorides for AACM 3 and PC concretes of similar strength are 1.65% and 3.2% by weight of binder respectively.

3. The chloride diffusion parameters C_0 and D_c of AACM concrete based on the water soluble (ws) and total bound (tb) chlorides give similar values. For example, the $(C_0)_{ws}$ and

$(C_0)_{tb}$ values of AACM 3 are 2.11% and 2.39%wt. of binder respectively at 180days chloride exposure. The corresponding $(D_c)_{ws}$ and $(D_c)_{tb}$ values are equal at all exposure periods. Hence water soluble (physically bound) chloride data is suitable for characterizing chloride diffusion of AACM concrete. This is contrary to the practice (and test standards) for conventional PC concrete where acid soluble (chemically bound) chloride data are used for characterizing C_0 and D_c. The test data on PC concrete in the paper also validate this practice.

4. The C_0 values of AACM concrete relating to both physically and chemically bound chlorides increase with chloride exposure period in a relationship of the form:

$$C_0 = C_{ref} + k\sqrt{t - t_{ref}}$$

Where C_0 is the surface chloride concentration at time *t*. C_{ref} is the surface chloride concentration corresponding to the reference time t_{ref} and *k* is constant.

The corresponding D_c values of AACM concrete decrease with longer chloride exposure period following the relationship:

$$D_C = D_{ref}\, t^{-m}$$

where: D_c is the apparent diffusion coefficient at time *t*, D_{ref} is diffusion coefficient at reference time t_{ref}, and m is the age factor ranging between 0.512 and 0.574 for the AACM concrete. The value of m decreases with decreasing molarity of the alkaline activator which reflects greater chloride diffusion with decreasing molarity of activator.

5. The long-term prediction model for D_c and C_0 (conclusion 4) can be used to predict long term chloride concentration in AACM concrete using either water soluble or total bound chloride data obtained at an early age. For example, the predicted water soluble and total bound chloride concentrations at 20years are 11.19% and 11.65% by weight of binder respectively in AACM 1 concrete.

6. The difference in chloride diffusion coefficient D_c of AACM and PC concrete of similar strength is greater at early age and reduces with age. This is reflected in the long term

predicted values of chloride concentrations. For example, the $(D_c)_{tb}$ at 55days chloride exposure are 6.5 x $10^{-12}m^2/s$ and 8.7 x $10^{-12}m^2/s$ for AACM 3 and PC concrete respectively and their corresponding values after 20years exposure period are 4.0 x $10^{-13}m^2/s$ and 5.36 x $10^{-13}m^2/s$.

7. The chloride diffusion in AACM concrete is controlled by its porosity. The pore refinement in AACM concrete aids lower diffusion of chloride. The chloride diffusion parameters C_0 and D_c are related to porosity as follows:

$(C_0)_{tb} = 0.0664e^{0.31(p)}$ with $R^2 = 0.98$

$(D_c)_{tb} = 5 \times 10^{-13}e^{0.25(p)}$ with $R^2 = 0.92$.

Where; $(C_0)_{tb}$ and $(D_c)_{tb}$ are the total surface chloride (% wt. of binder) and diffusion coefficient (m^2/s) respectively and p is the porosity (%).

ACKNOWLEDGMENTS

The authors gratefully acknowledge the support of the Materials and Engineering Research Institute, Sheffield Hallam University and the funding provided to the second author for postgraduate study by the Tertiary Education Trust Fund, Ministry of Education, Federal Republic of Nigeria. The authors also acknowledge the recent award by the UK - India Newton - Bhabha programme through funding provided by Innovate UK, EPSRC (EP/P026206/1) and the Government of India for research on AACMs.

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